

Shear-Induced Crystallization in Novel Long Chain Branched Polypropylenes by *in-situ* Rheo-SAXS and -WAXD

R. Somani, L. Yang, B. Hsiao (SUNY, Stony Brook), P. Agarwal (ExxonMobil Chemical Company, Baytown Polymers Center, Texas)
Beamline(s): X3A2

Introduction: A new class of long chain branched isotactic polypropylene (LCB-iPP) polymers prepared using proprietary metallocene technology exhibit improved melt strength and mechanical properties, such as flexural modulus and tensile yield strength. These LCB-iPPs have unique molecular architecture, i.e. significant population of highly branched chains in the high molecular weight tail of the molecular weight distribution. The effects of the LCB-iPP on shear-induced crystallization development was investigated using *in-situ* rheo-SAXS (small-angle X-ray scattering) and -WAXD (wide-angle X-ray diffraction) techniques. The results showed that upon application of a step shear (rate = 60 s^{-1} , $t_s = 0.25 \text{ s}$, $T = 140^\circ\text{C}$), the fraction of oriented crystals is substantially higher in the LCB-iPP compared to linear iPP. The value of Avrami exponent, n , ranged from 1.2 to 2.3 indicating a rod or disc-like crystal growth geometry during flow-induced crystallization. In addition, the crystallization kinetics of the branched polymer is enhanced by more than an order of magnitude compared to linear iPP under the same shear rate. The details of the crystalline phases determined from the WAXD data show that, in addition to monoclinic α -form crystals, there are triclinic γ -form crystals as well, which is attributed to the regio defects of the i-PP chain molecules.

Methods and Materials: Synchrotron X-ray measurements were carried using a Linkam CSS-450 high temperature shearing stage at the X3A2 Beamline; a 2D MAR CCD detector was used for the detection of 2D scattering patterns. The four isotactic polypropylene samples have different branching index (g), the lower values of g indicate higher level of long chain branching.

Results and Discussion: The SAXS patterns in Figure 1 clearly show that due to the oriented structures both SAXS intensities along the equator and the meridian increase with the branching level. The WAXD patterns of LCB 05, 07 and 13 samples show that the azimuthal breadths of crystal reflections are relatively narrow indicating that the crystal orientation is high. On the other hand, in linear iPP sample (LCB 01) the crystal orientation is relatively weak. The analysis of crystallinity data from WAXD using Avrami model indicate a rod- and disc-like crystal growth geometry in the branched samples and a spherulitic crystal growth geometry in the linear iPP polymer. Also, their crystallization kinetics is improved by more than an order of magnitude. The degree of branching in polymer molecules is expected to profoundly affect their relaxation behavior. As one might expect, at

a given temperature, the longest relaxation time, λ increases with the branching level. Thus, the highly branched molecules take a longer time for relaxation from orientation caused by the imposed flow conditions. In view of this, it is conjectured that the oriented segments of highly branched species take part in the formation of precursors of primary nuclei for crystallization of extended chain crystals. Our previous studies have shown that in iPP melts, even a small amount of the shish-like extended chain crystals induces nucleation and growth of a large amount of kebab-like crystal lamellae. The present results are consistent with the hypothesis that a large amount of linear nuclei for crystallization of extended chain crystals (rod-like) form immediately after shear and that highly branched molecules are more likely to form these nuclei due to their longer relaxation times. The chain-folded crystals grow radially outward from many nucleation sites along the length of nuclei. The formation of γ -phase is promoted, perhaps mainly due to the regio defects introduced during polymerization by the metallocene catalyst technology employed.

The strong crystal orientation and improved

crystallization kinetics in flow is attributed to the unique molecular architecture of the LCB-iPP polymers and its related effect on their broadened and complex relaxation behavior.

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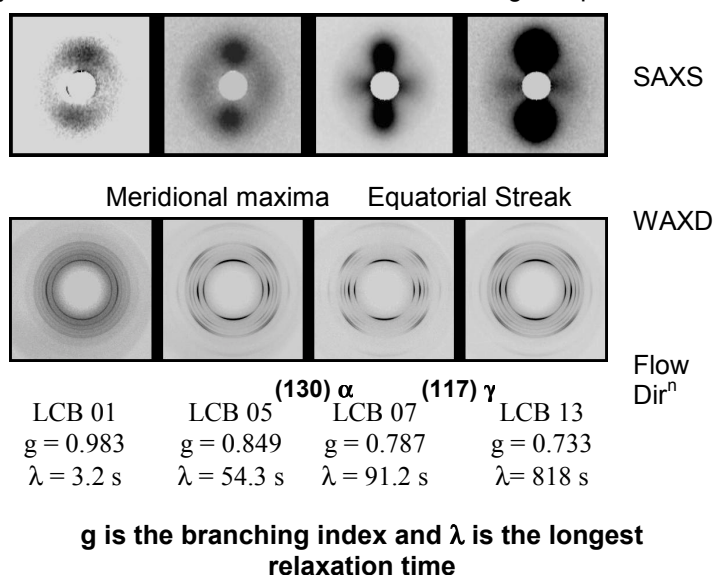


Figure 1: 2D SAXS patterns of the four LCB-iPP polymers 30 min after shear (shear rate = 60 s^{-1} , $t_s = 0.25 \text{ s}$, $T = 140^\circ\text{C}$).